

## MEASUREMENT OF PRESSURE EFFECTS ON N-HEXADECANE CRACKING RATES

Kenneth J. Jackson, Alan K. Burnham, Robert L. Braun, and Kevin G.  
Knauss

L-202, Earth Sciences Dept.  
Lawrence Livermore National Laboratory  
Livermore, CA 94550

Keywords: Hexadecane, cracking rates, pressure effects

### ABSTRACT

Experiments designed to determine the possible role of pressure in governing the kinetics of n-hexadecane (n-C<sub>16</sub>) cracking reactions were conducted in Dickson-type autoclaves at temperatures from 300 to 370 °C and pressures from 150 to 600 bars. Good agreement with published reaction kinetics was obtained at temperatures  $\geq 350$  °C. Values determined at lower temperatures indicate slower rates than predicted from earlier experiments and show a distinct induction period at 300 °C. The activation energy determined for this reaction is about 60 kcal/mole at  $T > 330$  °C, but it may exceed 70 kcal/mole at lower temperatures. Product hydrocarbon compounds lighter than n-C<sub>16</sub> seem to follow the single, first order reaction kinetics shown by the disappearance of n-C<sub>16</sub>. Hydrocarbons larger than n-C<sub>16</sub>, however, seem to follow a serial reaction of generation and subsequent destruction (including conversion to solid products) at high percentage conversion. Limited data suggest that the cracking rate of n-C<sub>16</sub> may have a small dependence on pressure.

### EXPERIMENTAL PROCEDURES

The high temperature/pressure cracking experiments were run in Dickson-type, gold bag autoclaves (Seyfried et al., 1987). In this apparatus, the reaction vessel comprises an approximately 250 ml capacity gold bag which is capped with a commercially pure titanium head. The Ti head is fitted with a Ti or Au capillary-lined stainless steel sampling tube that allows the experiment to be sampled periodically during the course of a run at *in situ* conditions. During the runs, the samples contact only Au and carefully passivated Ti. The Au bag assembly is inserted into a stainless steel pressure cell filled with de-ionized water that serves as the pressure medium. In

turn, this assembly is fitted into a furnace assembly, as described by Seyfried et al. (1987).

Starting materials for all runs were 98.75 wt % n-C<sub>16</sub> spiked with small amounts of naphthalene and phenanthrene (approximately 1.0 and 0.25 wt. %, respectively), which served as internal standards. Before the samples were loaded into the Au bags, high purity N<sub>2</sub> gas was bubbled through them for at least 30 minutes to remove any reactive gases (e.g., O<sub>2</sub>) that might be dissolved in the starting materials. The Au bag was partially filled with about 70 g of the hexadecane solution. The remaining space was filled with N<sub>2</sub> gas after emplacing the Ti head assembly. After the vessel was loaded, pressure was gradually increased. This collapsed the Au bag and expelled the N<sub>2</sub> gas in the head space; leaving only the hexadecane solution in the reaction vessel.

#### SAMPLING PROCEDURES

During the course of the run, the solution was periodically sampled by bleeding off a small amount (usually 1-2 g) of the experimental charge into gas-tight glass syringes. The initial samples were a single liquid phase, but later samples yielded two phases because a gas phase separated from the liquid as the sample cooled. The gas was stripped from the liquid phase using a He gas extraction method, and the two fractions were analyzed separately. Liquid samples were diluted in CS<sub>2</sub> and analyzed by gas chromatography. Fig. 1 shows a sample analysis of the reaction products obtained from Run 1 at 353 °C and 300 bars after 169.3 hours of reaction. Gas samples were injected directly into a gas chromatograph, and checked for air contamination using mass spectrographic analyses.

#### RESULTS

The matrix of experimental conditions investigated in this work is shown in Table 1. Temperatures ranged from 300 to 370 °C and pressures ranged from 150 bars to 600 bars. Within this range of physical conditions, the disappearance of n-C<sub>16</sub> was measured as a function of time (e.g., Fig. 2a). Exponential rates of disappearance of n-C<sub>16</sub> are consistent with a single first order reaction and yield rate parameters consistent with published values (see below). An exception to this is the significant induction period exhibited by the 300 °C experiment (Fig. 2b). In addition to the disappearance of n-C<sub>16</sub>, the rate of production of various classes of product phases was determined. For convenience in interpreting the data, the product

phases were separated into methane and four additional groups determined by their carbon numbers. These groups are arbitrarily defined as: C2-C4, C5-C9, C10-C15, and everything larger than C16. Fig. 3 shows that the rate of appearance of these products, when plotted as a function of the percent of hexadecane remaining in the solution, is essentially identical for all seven runs.

Rate constants for the reaction of hexadecane shown in Fig. 4 and 5 were determined using the KINETICS code of Braun and Burnham (1990). Based on results from these experiments, the cracking rate of n-C<sub>16</sub> may have a small dependence on pressure (Fig. 5). It is not possible to quantitatively assess the size of this effect based on results from these experiments, because there are only a limited number of runs at a single temperature and different pressures. The activation energy for this reaction is 60 kcal/mole at T > 330 °C, but it appears to be increasing at lower T. However, this proposed decrease in activation energy is based on a single experiment at 300 °C in which there is some evidence of a distinct induction period, as shown in Fig. 2b. The significant induction period may influence interpretation of previous kinetic studies based on low-temperature, low-conversion data (e.g., Domine, 1991).

The kinetics of the production of the C1, C2-C4, C5-C9 and C10-C15 groups of product compounds seem to follow the same single, first order reaction kinetics exhibited by the disappearance of the hexadecane. However, the > C16 products follow a serial reaction of generation and subsequent destruction at high percent conversion.

#### REFERENCES

- Braun, R. L. and A. K. Burnham (1990) KINETICS: A computer program to analyze chemical reaction data. UCID-21588 Rev. 1, Lawrence Livermore National Laboratory, Livermore, CA, 11 p.
- Domine, F. (1991) *Organic Geochemistry* 17, 619-634.
- Doue, F. and G. Guiochon (1968) *J. Chim. Phys -Chim. Biol.* 64, 395.
- Doue, F. and G. Guiochon (1969) *Can. J. Chem.* 47, 3477.
- Fabuss, B. M., J. O. Smith, R. I. Lait, A. S. Borsanyi, and C. N. Satterfield (1962) *Ind. Eng. Chem. Process Des. Dev.* 1, 293.
- Fabuss, B. M., J. O. Smith, and C. N. Satterfield, (1964) *Adv. Pet. Chem. Refin.* 9, 179.
- Ford T. J. (1986) *Ind. Eng. Chem. Fundam.* 25, 240-243.
- Groenendyk, H., E. J. Levy, and S. F. Sarner (1970) *J. Chromatogr. Sci.* 8, 115.

- Panchenkov, G. M., V. Ya. Baranov (1958) *Izv. Vyssh. Uchebn. Zaved., Neft Gaz.* 1, 703.
- Tilcheev, M. D. and K. I. Zimina (1956) *Khim. Tekhnol. Topl.* 8, 23.
- Voge, H. H. and G. M. Good (1949) *J. Am. Chem. Soc.* 71, 593.
- Seyfried, W. E., D. R. Janecky and M. E. Berndt (1987) Rocking autoclaves for hydrothermal experiments II. The flexible reaction-cell system. In *Hydrothermal Experimental Techniques* (G. C. Ulmer and H. L. Barnes, eds.) Wiley-Interscience, 216-237.

Run Number	T (°C)	P (bars)	Maximum Conv. (%)	Duration (hr)
1	353	300	77.3	764
2	330	150	22.8	1052
3	300	300	1.1	5615
4	329	480	5.4	1027
5	333	600	28.1	2397
6	369	250*	89.3	433
7	371	300*	88.7	315

Table-1. Experimental conditions, extent of reaction, and run duration for the seven experiments described in this work. \*Near the end of Runs 6 and 7, pressure increased to 283 and 343 bars, respectively.

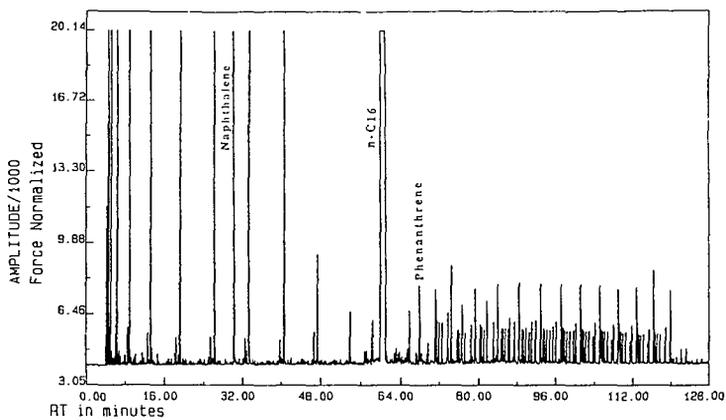


Figure 1. Sample gas chromatography trace showing the composition of the liquid phase in Run 1 (353 °C and 300 bars) at 169.3 hr elapsed time.

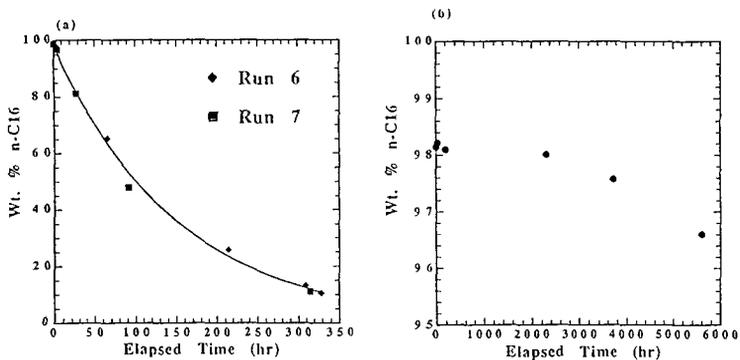


Figure 2. The disappearance of n-C<sub>16</sub> as a function of elapsed time (a) in Runs 6 and 7 (370 °C) and (b) in Run 3 (300 °C). The symbols are experimental values, and the curve represents an exponential curve fit through the points.

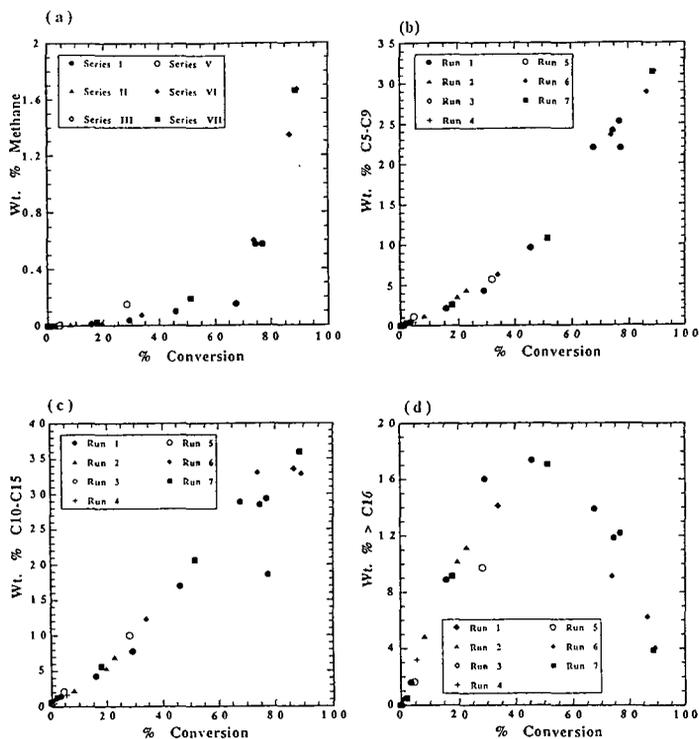


Figure 3. The appearance of product phases for all seven experiments as a function of % conversion of n-C16: (a) the appearance of methane, (b) the appearance of the C5 to C9 fraction, (c) the appearance of the C10 to C15 fraction, and (d) the appearance and subsequent disappearance of the > C16 fraction.

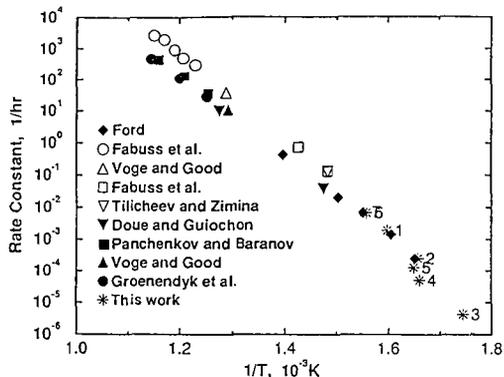


Figure 4. Comparison of hexadecane cracking rates compiled by Ford (1986) with values determined in this study. The numbered points correspond to run numbers listed in Table 1.

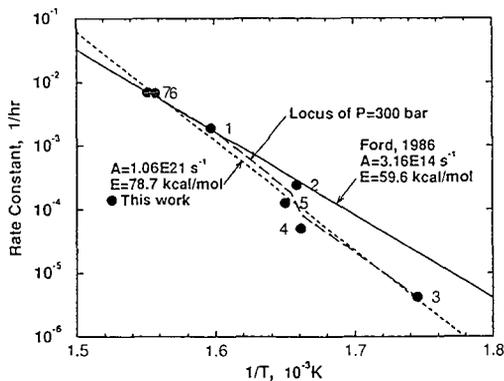


Figure 5. An enlargement of the lower right hand portion of Figure 4. The solid line shows an extrapolation of the activation energy and frequency factors determined by Ford (1986). The dotted line is a linear least squares fit through the rate constants determined in this work. The dashed line defines a locus of points consistent with the trace of a 300 bar isobar suggested by the data in this study.